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GAS PHASE PRODUCTION OF NHD$_2$ IN L134N

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ABSTRACT

We show analytically that large abundances of NH$_2$D and NHD$_2$ can be produced by gas phase chemistry in the interiors of cold dense clouds. The calculated fractionation ratios are in good agreement with the values that have been previously determined in L134N and suggest that triply-deuterated ammonia could be detectable in dark clouds. Grain surface reactions may lead to similar NH$_2$D and NHD$_2$ enhancements but, we argue, are unlikely to contribute to the deuteration observed in L134N.

Subject headings: ISM: individual objects: L134N – ISM: chemistry – ISM: deuterium

1. INTRODUCTION

Recently NHD$_2$ and NH$_2$D were detected in L134N by Roueff et al. (2000). This is the first detection of a doubly-deuterated molecule in a dark interstellar cloud. Roueff et al. derived fractionation ratios of $R(\mathrm{NH_2D}) = 0.1$ and $R(\mathrm{NHD_2}) = 0.05$, where we define the fractionation ratio, R, of the deuterated species XH$_m$D$_{m'}$ to be $n(\mathrm{XH}_m\mathrm{D}_{m'})/n(\mathrm{XH}_{m+1}\mathrm{D}_{m'-1})$ where n is the number density. NH$_2$D was previously detected at the same position by Olberg et al. (1985) and Saito et al. (2000), who determined $R(\mathrm{NH_2D}) \approx 0.05$. The first interstellar detection of N$_2$D$^+$ was also made at approximately the same location by Snyder et al. (1977), who derived $R(\mathrm{N_2D^+}) = 0.45$. DCO$^+$ has been detected in L134N by Wootten, Loren, & Snell (1982), Guélin, Langer, & Wilson (1982), and Butner, Lada, & Loren (1995) with values for $R(\mathrm{DCO^+})$ in the range 0.03–0.07. More recent observations of N$_2$D$^+$ and DCO$^+$ at the same location as the NHD$_2$ peak were carried out by Tiné et al. (2000), who obtained fractionation ratios of 0.35 and 0.18 respectively for these ions. In addition to the deuterium fractionation, it is known that the absolute abundances relative to H$_2$ of NH$_3$ and N$_2$H$^+$ peak at the same position (Ungerechts, Walmsley, & Winnewisser 1980; Swade 1989; Dickens et al. 2000).

The only other doubly deuterated molecule observed in the interstellar medium is D$_2$CO, which has been detected in two regions: the well-known Orion Compact Ridge source (Turner 1990) and the low-mass protostar IRAS 16293-2422 (Ceccarelli et al. 1998; Loinard et al. 2000). In both cases, the large D$_2$CO fractionation – $R(\mathrm{D_2CO}) = 0.02$ and 0.35 respectively – is thought to result from grain surface chemistry, since the molecular abundances in these warm regions reflect the evaporation of ice mantles from interstellar dust grains (e.g. Brown, Charnley, & Millar 1988), and the post-evaporation molecular D/H ratios remain equal to the ratios in the precursor ices for over 10^4 years (Rodgers & Millar 1996). Deuterated formaldehyde forms on grains via addition of H and D atoms to CO (Tielens 1983; Charnley, Tielens, & Rodgers 1997), and so large amounts of HDCO and D$_2$CO can be expected if the gas-phase atomic D/H ratio is large. NH$_2$D and NHD$_2$ can also form on grains through D and H atom additions to atomic N (Brown & Millar 1989). However, as noted by Roueff et al. (2000), the lack of on-

going star formation, together with the low temperature in L134N ($T \approx 9$–12 K; Swade 1989; Dickens et al. 2000), suggests that mantle removal has not occurred. Markwick, Millar, & Charnley (2000) have proposed a nonthermal mechanism for removing grain mantles in dark clouds involving ion-neutral streaming produced in MHD motions. However, this process also acts to remove H$_2$D$^+$ and N$_2$D$^+$ from the gas (Charnley 1998) and so this mechanism is unlikely to have occurred at the deuterium emission peak in L134N. It therefore appears that the NH$_2$D and NHD$_2$ observed in L134N must be created in the gas phase.

In this paper, we address the issue of gas phase ammonia deuteration. We first discuss the underlying chemistry which controls the deuterium fractionation and ammonia abundances in dark clouds. We then show how successive deuteron transfer reactions can lead to large abundances of multiply-deuterated ammonia. We derive analytical expressions for the steady-state D/H ratios in isotopomers of ammonia, and compare these theoretical ratios with those observed in L134N and with those expected from grain surface chemistry.

2. DEUTERIUM FRACTIONATION IN DARK CLOUDS

A number of singly-deuterated molecules have been detected in dark interstellar clouds with large fractionations ($R \sim 0.001$–0.1), and the theory behind the observed D enhancement is well understood (e.g. Watson 1974; Guélin et al. 1982; Millar, Bennett, & Herbst 1989; Roberts & Millar 2000). Essentially, small zero-point energy differences ensure that molecular ions become preferentially deuterated via D/H exchange reactions with HD, and subsequent ion-molecule reactions spread this D-enrichment to neutral species. At 10 K, the most important fractionation process is that of H$_2$D$^+$:

$$\mathrm{H_3^+} + \mathrm{HD} \;\rightleftharpoons\; \mathrm{H_2D^+} + \mathrm{H_2} \qquad (1)$$

We can quantify the degree of fractionation attainable by reaction (1) by writing

$$R(\mathrm{H_2D^+}) = \mathcal{S}R(\mathrm{HD}) \qquad (2)$$

where $R(\mathrm{HD})$ will be twice the cosmic D/H ratio of $\approx 1.6 \times 10^{-5}$ (Linsky et al. 1995), and $\mathcal{S}$ is the so-called en-

hancement factor, given by:

$$\mathcal{S} = \frac{k_f}{k_r \; + \; \sum_j k_j x(m_j) \; + \; \alpha_e(\mathrm{H_2D^+})x_e} \quad (3)$$

(Stark, van der Tak, & van Dishoeck 1999; Millar et al. 2000). k_f and k_r are the forward and reverse rate coefficients for reaction (1); at $10\,\mathrm{K}$ the respective values are 1.7×10^{-9} and 3.6×10^{-18} cm^{3}s^{-1} (Millar et al. 1989; Sidhu, Miller, & Tennyson 1992), x_e is the electron fraction, k_j is the rate coefficient for proton or deuteron transfer to species m_j (principally CO, $\mathrm{N_2}$ and O) whose abundance is $x(m_j) \equiv n(m_j)/n(\mathrm{H_2})$, and $\alpha_e(\mathrm{H_2D^+})$ is the electron dissociative recombination coefficient of $\mathrm{H_2D^+}$ (equal to 6×10^{-8} $(T/300\,\mathrm{K})^{-0.65}$ cm^{3}s^{-1}; Larsson et al. 1996).

Proton transfer from $\mathrm{H_3^+}$ to CO and $\mathrm{N_2}$ is the primary source of the HCO$^+$ and $\mathrm{N_2H^+}$ ions, so the $\mathrm{H_2D^+}$ enhancement also determines the fractionation of DCO$^+$ and $\mathrm{N_2D^+}$. If we assume that one third of such reactions result in deuteron transfer, it follows that

$$R(\mathrm{DCO^+}) = R(\mathrm{N_2D^+}) = \tfrac{1}{3}R(\mathrm{H_2D^+}) = \tfrac{1}{3}\mathcal{S}\,R(\mathrm{HD}) \quad (4)$$

This simple theory predicts that the fractionation of $\mathrm{N_2D^+}$ and DCO$^+$ should be equal. However, as discussed in §1, the values measured in L134N by Tiné et al. (2000) are 0.35 and 0.18 respectively. This discrepancy is puzzling, since if anything, the value of $R(\mathrm{DCO^+})$ should be larger than $R(\mathrm{N_2D^+})$ as DCO$^+$ is also fractionated via the reaction of HCO$^+$ with atomic D (Adams & Smith 1985; cf. Dalgarno & Lepp 1984; Opendak 1993). A possible explanation is that deuteron transfer from $\mathrm{H_2D^+}$ to $\mathrm{N_2}$ occurs preferentially to proton transfer, but that the branching ratios for $\mathrm{H_2D^+} + \mathrm{CO}$ are statistical. Nevertheless, the $\mathrm{N_2D^+}$ fractionation is comparable to that determined by Snyder et al. (1977) and, to order of magnitude, the observed fractionation is compatible with the above theory if $\mathcal{S} \gtrsim 10^4$.

3. GAS PHASE AMMONIA FORMATION

The observed ammonia abundance in L134N is $\sim 10^{-7}$ (Swade 1989; Dickens et al. 2000), in agreement with the steady-state value in chemical models where most of the nitrogen is in molecular form (e.g. Millar, Farquhar, & Willacy 1997). In this case, ammonia formation is initiated by He$^+$ attack on $\mathrm{N_2}$ to form N$^+$. This ion then undergoes successive reactions with $\mathrm{H_2}$ until $\mathrm{NH_4^+}$ is formed, which then recombines to give $\mathrm{NH_3}$:

$$\mathrm{N_2} \xrightarrow{\mathrm{He^+}} \mathrm{N^+} \xrightarrow{4\mathrm{H_2}} \mathrm{NH_4^+} \xrightarrow{e^-} \mathrm{NH_3} \quad (5)$$
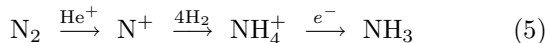
This formation mechanism remains somewhat controversial, because the first hydrogenation step

$$\mathrm{N^+} + \mathrm{H_2} \longrightarrow \mathrm{NH^+} + \mathrm{H} \quad (6)$$
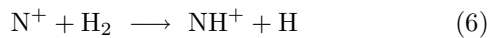
is endothermic by $\approx 170\,\mathrm{K}$ (Marquette, Rebrion, & Rowe 1988). However, this is slightly less than the ground state rotational energy of ortho-$\mathrm{H_2}$, and Le Bourlot (1991) showed that as long as the ortho-to-para ratio is greater than $\sim 10^{-4}$ then reaction (6) is the dominant loss route for N$^+$, so reaction sequence (5) proceeds efficiently. Even

at $10\,\mathrm{K}$, chemical cycling between ortho and para-$\mathrm{H_2}$ via proton transfer reactions is able to provide sufficient ortho-$\mathrm{H_2}$ (Le Bourlot 1991, 2000).

At the densities appropriate for L134N, gas phase chemistry, rather than freeze-out onto grains, is the dominant loss route for ammonia. Cosmic ray ionization of $\mathrm{H_2}$ followed by successive proton transfer reactions results in $\mathrm{NH_3}$ molecules being recycled into $\mathrm{NH_4^+}$ ions, which can then recombine to either $\mathrm{NH_3}$ or $\mathrm{NH_2}$. In the latter case, the $\mathrm{NH_2}$ is rapidly destroyed by atomic oxygen. The resulting expression for the steady-state ammonia abundance is:

$$x(\mathrm{NH_3}) = \frac{0.3\epsilon\zeta x(\mathrm{He})x(\mathrm{N_2})}{(1 - \epsilon)[x(\mathrm{CO}) + x(\mathrm{N_2})]\Gamma_{\mathrm{H^+}}} \quad (7)$$

where ϵ is the fraction of $\mathrm{NH_4^+}$ dissociative recombinations that lead to $\mathrm{NH_3}$, ζ is the cosmic ray ionization rate, and $\Gamma_{\mathrm{H^+}}$ is the total rate (s^{-1}) for proton transfer to $\mathrm{NH_3}$. In theory, $\Gamma_{\mathrm{H^+}}$ will depend on the abundances of all molecular ions capable of transferring a proton to ammonia, but because HCO$^+$, $\mathrm{N_2H^+}$ and $\mathrm{H_3^+}$ are the dominant ions we can write

$$\Gamma_{\mathrm{H^+}} \approx 10^{-9}\,[2.2n(\mathrm{HCO^+}) + 2.3n(\mathrm{N_2H^+}) + 2.7n(\mathrm{H_3^+})] \quad (8)$$

Based on the fact that the abundances of HCO$^+$ and $\mathrm{N_2H^+}$ are observationally well-determined in L134N, and that the abundance of $\mathrm{H_3^+}$ can be obtained from simple chemical arguments (see §5), we derive $\Gamma_{\mathrm{H^+}} \approx 10^{-12}$ s^{-1}. The value of ϵ was measured in the laboratory by Vikor et al. (1999), and was found to be 0.69. With assumed values for $x(\mathrm{He}) = 0.15$, and $\zeta = 1.3 \times 10^{-17}$ s^{-1}, the observed ammonia abundance in L134N can be reproduced by equation (7) if the $\mathrm{N_2/CO}$ ratio is ≈ 0.1, consistent with the $\mathrm{N_2}$ abundances determined in a number of dark clouds by Womack, Ziurys, & Wyckoff (1992b).

4. GAS PHASE AMMONIA FRACTIONATION

We have extended our steady-state analysis to include multiply deuterated ammonia. Figure 1 shows the primary chemical reactions creating and destroying $\mathrm{NH_3}$ and its associated isotopomers through ion-molecule reactions involving generic protonated and deuterated ions, XH$^+$ and XD$^+$. After $\mathrm{NH_3}$ is formed by the reaction sequence (5), deuteron transfer reactions form $\mathrm{NH_3D^+}$ which can then recombine to give $\mathrm{NH_2D}$. Successive deuteron transfer reactions can lead eventually to $\mathrm{NHD_2}$ and $\mathrm{ND_3}$. The relative steady-state abundances therefore depend on the XD$^+$/XH$^+$ ratio and the branching ratios for dissociative recombination of the deuterated ions.

We can quantify the XD$^+$/XH$^+$ ratio by introducing the parameter $\bar{R}$, equal to the ratio of the rates for deuteron vs. proton transfer, i.e. we define $\bar{R} \equiv \Gamma_{\mathrm{D^+}}/\Gamma_{\mathrm{H^+}}$, where $\Gamma_{\mathrm{H^+}}$ is given by equation (8) and $\Gamma_{\mathrm{D^+}}$ is obtained from

$$\Gamma_{\mathrm{D^+}} \approx 10^{-9}\,[2.2n(\mathrm{DCO^+}) + 2.3n(\mathrm{N_2D^+}) + 0.9n(\mathrm{H_2D^+})] \quad (9)$$

As with $\Gamma_{\mathrm{H^+}}$, there will also be a small contribution to $\Gamma_{\mathrm{D^+}}$ from isotopomers of less abundant ions (e.g. $\mathrm{H_3O^+}$, HOCO$^+$, HCNH$^+$, etc.), but because HCO$^+$ is the most abundant ion, and because the deuterium fractionation in
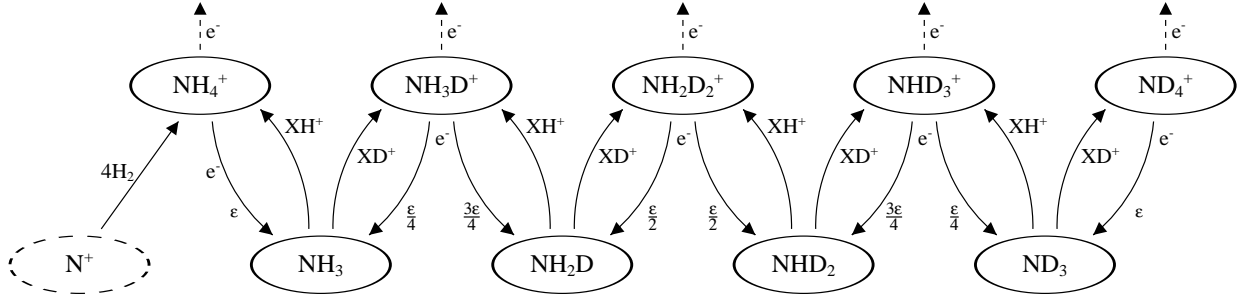
FIG. 1.— Reaction network for ammonia deuteration in cold clouds. XH^+ and XD^+ represent all species capable of transferring a proton or deuteron to NH_3; principally H_3^+, N_2H^+, HCO^+, and their deuterated isotopomers. Also shown are the assumed statistical branching ratios for each dissociative recombination channel. ϵ is the fraction of dissociative recombinations which result in an isotopomer of NH_3 rather than NH_2.

these minor ions originates with deuteron transfer from H_2D^+ and DCO^+, in practice $\bar{R} \approx R(DCO^+)$.

We assume that the NH_3/NH_2 branching ratio, ϵ, is the same for deuterated ammonium ions as for NH_4^+, and we assume statistical branching ratios regarding the position of the D in the products (see Fig. 1). Gellene & Porter (1984) measured the branching ratios for electron dissociative recombination of NHD_3^+ and found H atom ejection occurred 2.7 times more frequently than D ejection, implying that the N–H bonds are eight times more likely to break than the N–D bond. A similar effect has been observed in the recombination of HDO^+ and HD_2O^+ (Jensen et al. 1999, 2000). Therefore, our results represent a lower limit to the amount of deuteration that can occur via ion-molecule chemistry, since preferential retention of the D in the molecule is more likely to occur.

For each of the species in Fig. 1, one can write an expression equating the formation and destruction rates. These expressions can then be solved to give the number density ratios at steady state. After some algebra one obtains:

$$R(ND_3) = \frac{\epsilon \bar{R}}{(4 - \epsilon) + (4 - 4\epsilon)\bar{R}} \quad (10)$$

$$R(NHD_2) = \frac{2\epsilon \bar{R}}{(4 - 2\epsilon) + (4 - 3\epsilon)\bar{R} - 3\epsilon R(ND_3)} \quad (11)$$

$$R(NH_2D) = \frac{3\epsilon \bar{R}}{(4 - 3\epsilon) + (4 - 2\epsilon)\bar{R} - 2\epsilon R(NHD_2)} \quad (12)$$

Note that, although the *absolute* abundances will depend on the formation rate of NH_3, the *relative* abundances of the deuterated forms depend only on $\bar{R}$ and ϵ, and so are not affected by any uncertainty regarding the kinetics of ammonia synthesis.

Solutions of equations (10)–(12) are plotted in Figure 2. For $\bar{R} \lesssim 1$ the predicted values are proportional to $\bar{R}$. At larger values of $\bar{R}$ the curves asymptotically approach the value determined by the branching ratios of the deuterated ammonium ions. The shaded region in Fig. 2 covers the observed range in $\bar{R}$; from a lower bound of 0.05 inferred from DCO^+ observations (see §1), up to a maximum of 0.35 implied by the N_2D^+ observations of Tiné et al. (2000). The filled circles in Fig. 2 show the observed NH_2D and NHD_2 ratios; the fact that both the observed

values imply the *same* underlying value of $\bar{R}$ is convincing evidence that gas-phase chemistry is the source of the NH_2D and NHD_2 in L134N.

Note that there also exists another gas phase route to singly-deuterated ammonia: the reaction of N^+ with HD, analogous to reaction (6). In this case, the channel leading to $ND^+ + H$ is favored over $NH^+ + D$, since the endothermicity of the former channel is only 16 K (Marquette et al. 1988). Hence, if the H_2 ortho-to-para ratio is low so that reaction (6) occurs slowly, this can lead to large enhancements of NH_2D via the deuterated version of reaction sequence (5) (Tiné et al. 2000). However, this mechanism cannot explain the presence of doubly-deuterated ammonia. As we have shown that deuteron transfer reactions are more than capable of producing the observed NH_2D and NHD_2 abundances, we believe that the scheme illustrated in Fig. 1 is sufficient to explain the ammonia deuteration in L134N.

5. THE CHEMICAL STATE OF L134N

We have shown that the observed abundances of ammonia isotopomers in L134N are consistent with the steady-state solutions of a relatively simple ion-molecule reaction scheme (see Fig. 1), if the value of $\bar{R} \approx 0.1$. In order to assess the validity of our analysis, we would like to be able to reconcile our scheme with the observed abundances of simple molecular ions and their deuterated counterparts.

The observed range of values for $\bar{R}$ implies a value of $\mathcal{S}$ of 5000–35000 (eqn. [4]). In order to calculate the expected value of $\mathcal{S}$ in L134N from equation (3), we need to know the electron fraction, x_e, and $\sum_j k_j x(m_j)$, the total removal rate of H_2D^+ through reactions with heavy species. We can calculate these values approximately from the the steady-state H_3^+ concentration, which is given by

$$n(H_3^+) = \frac{\zeta}{\sum_j k_j x(m_j) + \alpha_e(H_3^+)x_e + k_f R(HD)} \quad (13)$$

and the charge conservation equation:

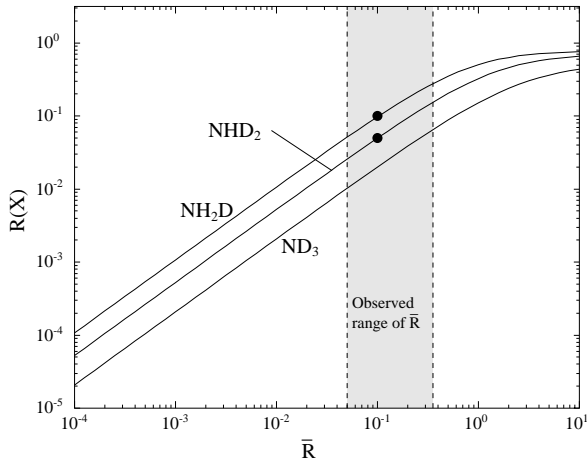$$x_e \approx x(HCO^+) + x(N_2H^+) + x(H_3^+) \quad (14)$$

Fig. 2.— Steady-state fractionation ratios for deuterated ammonia isotopomers, as a function of the mean deuterium fractionation in molecular ions, $\bar{R}$. The curves correspond to solutions of equations (10)–(12) for $\epsilon = 0.69$, the filled circles show the observed values of $R(\mathrm{NH_2D})$ and $R(\mathrm{NHD_2})$, and the shaded region illustrates the range of values of $\bar{R}$ implied by different observations.

Note that the rate coefficients in equation (13) are the same as in equation (3), since we assume that $\mathrm{H_2D^+}$ reacts at the same rate as $\mathrm{H_3^+}$, except for electron recombination, where we use the value for $\alpha_e(\mathrm{H_3^+})$ of $1.15 \times 10^{-7}(T/300\,\mathrm{K})^{-0.65}$ measured by Sundström et al. (1994).

HCO$^+$ and N$_2$H$^+$ have been observed in L134N, and their respective abundances are 1.2×10^{-8} and 7×10^{-10} (Swade 1989; Womack et al. 1992a; Dickens et al. 2000). Adopting physical parameters of $T = 10\,\mathrm{K}$ and $n(\mathrm{H_2}) = 2 \times 10^4\,\mathrm{cm^{-3}}$ (Dickens et al. 2000), we thus have three equations ([3], [13], and [14]) in three unknowns (x_e, $x(\mathrm{H_3^+})$, and $\sum_j k_j x(m_j)$). Solving these equations for different values of $\mathcal{S}$ allows us to constrain the chemical state of L134N. Also, because the rate coefficients for reactions of $\mathrm{H_3^+}$ and $\mathrm{H_2D^+}$ with heavy molecules are $\approx 2 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$, we can calculate the total abundance of heavy molecules from our derived value of $\sum_j k_j x(m_j)$.

For $\mathcal{S} = 5000$, we calculate $x_e = 1.4 \times 10^{-8}$, $x(\mathrm{H_3^+}) = 1.6 \times 10^{-9}$, and $\sum_j x(m_j) = 1.6 \times 10^{-4}$, consistent with little depletion of CO, N$_2$, and O from the gas phase. On the other hand, for $\mathcal{S} = 35000$, we derive $x_e = 1.9 \times 10^{-8}$, $x(\mathrm{H_3^+}) = 6 \times 10^{-9}$, and $\sum_j x(m_j) = 1.9 \times 10^{-5}$, implying significant depletion. For the intermediate value of $\mathcal{S} \approx 10^4$ inferred from the deuterated ammonia fractionation, we find that partial depletion ($\sim 50\%$) of heavy molecules is required to account for the observed deuterium enhancements. A similar conclusion has been reached by Roberts & Millar (2000). Finally, as our calculated ionization levels lead to good agreement with the observed NH$_3$ abundance (§3), we conclude that the observed abundances and fractionations in L134N are well-matched by steady-state ion-molecule chemistry.

6. GAS PHASE VS. GRAIN SURFACE AMMONIA FRACTIONATION

Despite reservations concerning the physical conditions in L134N, some as yet unidentified mechanism may be returning mantle-formed molecules to the gas there. The mantle abundances of ammonia isotopomers computed numerically by Brown & Millar (1989) (see their table 2) effectively rule out a grain surface origin when scaled to the ammonia abundance in L134N. However, their surface reaction scheme permits larger D/H ratios than those presented, since the fractionation is proportional to the gas phase atomic D/H ratio, $R(\mathrm{D})$, which may be higher than the value assumed in their calculations. Following the scheme of Brown & Millar, we can derive values for the surface fractionation ratios:

$$R_s(\mathrm{NH_2D}) = \tfrac{3}{\sqrt{2}} R(\mathrm{D}) \tag{15}$$

$$R_s(\mathrm{NHD_2}) = \tfrac{1}{\sqrt{2}} R(\mathrm{D}) \tag{16}$$

$$R_s(\mathrm{ND_3}) = \tfrac{1}{3\sqrt{2}} R(\mathrm{D}) \tag{17}$$

Thus, if $R(\mathrm{D}) \approx 0.05$, then it is also possible to explain the observed abundances by surface formation of ammonia.

It may be possible, however, to discriminate between alternative formation mechanisms by examining the relative scaling of the fractionation ratios. For example, grain surface formation implies that

$$R_s(\mathrm{NH_2D}) : R_s(\mathrm{NHD_2}) : R_s(\mathrm{ND_3}) = 1 : 0.33 : 0.11 \tag{18}$$

whereas, to first order, gas phase chemistry implies (using equations [10]–[12])

$$R(\mathrm{NH_2D}) : R(\mathrm{NHD_2}) : R(\mathrm{ND_3}) = 1 : 0.49 : 0.19 \tag{19}$$

The fact that the calculated values of R for the three isotopomers always have the same ratio irrespective of their absolute values is apparent from Fig. 2, where the vertical separation of the curves for the three isotopomers is constant.

For doubly-deuterated ammonia, the predicted ratios are similar, with the observed value of $R(\mathrm{NH_2D}) = 0.1$ implying respective values of $R(\mathrm{NHD_2}) = 0.05$ and 0.03

for gas phase and surface chemistry. Although the observed value of 0.05 agrees with our gas phase scheme, the observational uncertainties are too large to rule out surface formation. However, for triply-deuterated ammonia, the gas phase scheme predicts a fractionation almost twice as large; when scaled to the NH_3 abundance this implies a ND_3/NH_3 ratio 2.5 times greater than the value predicted by surface chemistry (where we have used the relation $ND_3/NH_3 = R(ND_3) \times R(NHD_2) \times R(NH_2D)$; cf. our definition of R in §1). With the observed values $x(NH_3) = 10^{-7}$ and $R(NH_2D) = 0.1$, we predict $x(ND_3) \approx 10^{-11}$. Hence, if ND_3 can be detected (or an upper limit determined) in L134N, it may be possible to determine whether the ammonia is formed in the gas or on the grains.

It is worth stressing that the kind of scaling relations for multiply-deuterated fractionation ratios expressed by equations (18) and (19) are applicable in general to all molecules. Thus, whereas the fractionation of singly-deuterated molecules reflects both the formation mechanism of the molecule and the underlying D/H ratio in the precursors, the relative fractionation ratios of multiply-deuterated molecules reflect only the formation mechanism. This fact was first appreciated by Turner (1990), who used the D_2CO:$HDCO$:H_2CO ratios to show that formaldehyde in the Orion Compact Ridge should have a grain surface origin.

7. DISCUSSION

We have shown that large abundances of NH_2D and NHD_2 can be produced by gas phase chemistry in the interiors of cold dense clouds. Ammonia is deuterated via deuteron transfer from species such as H_2D^+, DCO^+, and N_2D^+, followed by dissociative recombination. This mechanism is able to match the observed fractionation ratios of both species if the underlying XD^+/XH^+ ratio, $\bar{R}$, equals 0.1.

Grain surface formation of ammonia produces distinct fractionation ratios, however the uncertainties in the observed abundances mean that we cannot definitively conclude that deuterated NH_3 is being formed in the gas. Because the scaling of the fractionation ratios expected from these two processes is not the same, this raises the possibility that the NH_2D:NHD_2:ND_3 ratios may ultimately be used to determine the origin of these molecules. In particular, this could be resolved with the detection of ND_3, which we predict to have an abundance of $\sim 10^{-11}$ in L134N. Gas phase formation appears more feasible than surface chemistry since it is able to account for the observed NH_3 abundance without recourse to uncertain surface processes and desorption mechanisms. A further problem for the grain surface hypothesis is the fact that the large value of $R(NH_2D)$ in L134N requires a gas phase atomic D/H ratio of 0.05, but theoretical models predict an equilibrium value of only a few times 10^{-3} at $10\,K$ (Millar et al. 1989; Roberts & Millar 2000).

We also find that the large observed molecular D/H ratios can only be reproduced if heavy elements are partially depleted onto grain surfaces. Therefore, it appears that the deuterium emission peak in L134N traces a small region where significant amounts of CO, N_2 and O are frozen onto grains. A similar region of enhanced D fractionation is known to exist in TMC-1 (Guélin et al. 1982), a dark cloud that appears to be physically similar to L134N. The fact that there appear to be several infrared sources located behind L134N (Snell 1981) may allow the molecular depletion into ice mantles to be measured and crudely mapped. Alternatively, these spatial gradients may be due to the energy available when ions and neutrals have slightly different velocities. In this case, k_r becomes the dominant term in the denominator of the expression for $\mathcal{S}$ (eqn. [3]), which is consequently reduced (Charnley 1998). Another explanation may be the existence of chemical bistability in interstellar clouds; Gerin et al. (1997) showed that molecular D/H ratios are typically reduced by a factor of ten in the high ionization phase steady-state solution, as opposed to the low ionization phase.

Nevertheless, it seems more likely that depletion is the cause of the high deuteration in L134N, since the latter mechanisms act to reduce $\mathcal{S}$ whereas depletion causes $\mathcal{S}$ to increase. It is interesting to note that the observed range of $\bar{R}$ in L134N is always $\gtrsim 0.05$; this is what one would expect for a $10\,K$ cloud with no depletion, and is in fact the value derived from DCO^+ observations of a large number of cold clouds (Guélin et al. 1982; Butner et al. 1995). The fact that the fractionation in L134N is determined to be above this canonical cold cloud value is evidence for selective deuterium enhancement in this particular region, as opposed to a reduction of the fractionation in the surrounding gas. On the other hand, Gerin et al. (1997) observed a value of $R(DCO^+) = 0.003$ in the high latitude cloud MCLD 123.5+24.9, ten times lower than the 'normal' value. In this instance, it would appear that some mechanism is indeed operating to suppress the D/H enhancement.

If the depletion is particularly large, the value of $\bar{R}$ can become as large as unity (Millar et al. 2000). In this case, chemical models predict large abundances of HDCO and D_2CO (Roberts & Millar 2000), so it may be fruitful to search for D_2CO in dark clouds. Note, however, that deuterated formaldehyde may not in fact be as abundant as predicted by these models where it is assumed that H_2CO is deuterated via the same mechanism as NH_3, namely deuteron transfer from H_2D^+, DCO^+ etc. followed by dissociative recombination. In fact, the lowest energy isomer of protonated formaldehyde has the form H_2COH^+, and this ion has been detected in the interstellar medium (Ohishi et al. 1996). We may therefore expect that deuteron transfer to H_2CO will most likely result in H_2COD^+ and will not lead to HDCO after dissociative recombination (Sen, Anicich, & Federman 1992).

Finally, we note that the DCO^+ fractionation of 0.05 observed in a number of sources by Butner et al. (1995) is only a factor of two less than the value of $\bar{R}$ required to explain the ammonia deuteration in L134N. Therefore, multi-deuterated ammonia may be widespread in dark clouds.

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